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AN EXPERIMENTAL EVALUATION OF THE FLAMMABILITY AND PERFORMANCE POTENTIALS OF TWO AZEOTROPIC REFRIGERANT MIXTURES

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Abstract

The phaseout of CFC and HCFC refrigerants requires determination of substitute refrigerants for use in domestic heat pumps and refrigerators. This paper presents both flammability and heat pump performance test results of two azeotropic refrigerant mixtures of R-134a (1,1,1,2-tetrafluoroethane) with R-290 (Propane) and R-600a (Isobutane): R-290/134a (45/55), R-134a/600a (80/20). The flammability limit of R-290/134a is found as 2.9-11.0 % by volume. And that of R-134a/600a is 3.9-13.3 % by volume. Although the azeotropic mixtures remain flammable, they are less than their pure hydrocarbon components. The performance characteristics are compared with pure R-12, R-22, R-134a, and R-290 at test conditions including cases using liquid-line/suction-line heat exchange. In most cases, the coefficients of performance of the azeotropic mixtures are higher than that of R-12 and R-134a. In every case, the capacity for R-290/134a is higher than that for R-22. Also, the system capacity for R-134a/600a is higher than that for R-12 and R-134a. Results show that the discharge temperature for the azeotropic mixtures is always lower than that for the other refrigerants.

1. INTRODUCTION

In the search for alternative refrigerants, emphasis has been put on finding safe (i.e., nonflammable and nontoxic), chlorine-free single component fluids with similar vapor pressures to that which is intended to be replaced. The most successful, to date, has been the development of HFC-134a as an alternative to CFC-12. However, even this alternative has its limitations if it is intended as a 'drop-in' for existing CFC-12 machines. Most significant is the lack of mineral oil solubility with this or any other chlorine-free refrigerant, thus ester based lubricants has been developed recently. Also this ethane based alternative has, inherently, a steeper vapor pressure curve on a pressure-temperature diagram than the methane based CFC-12. The HCFC-22 alternative search is far more difficult, with no known single component fluid having a reasonably close vapor pressure curve. As a result, the craft of mixing two or more components to obtain all the desired working fluid properties has become popular.

Among the different types of mixtures, azeotropes are preferred because they remain at a constant temperature and composition throughout phase change; consequently they are not different from single component refrigerants for all practical purposes. However, virtually all of the halogenated hydrocarbon pairs have been identified (Morrison & McLinden, 1993) and so it is interesting to explore halogen and hydrocarbon pairs to determine if any of their azeotropes can match the performance of those slated for elimination. Incorporating a hydrocarbon within an azeotrope is likely to offer the additional advantage of making the mixture soluble with mineral oil. Thus, if this type of azeotrope has a similar performance as the refrigerant it is replacing, it could act as a true 'drop-in'. Of course, the disadvantage of using a high percentage of hydrocarbon in any mixture is that it is likely to be flammable. Although current practice does not include the use of flammable refrigerants for residential or commercial applications, several manufacturers are considering the possibility of doing so for hermetic (particularly sealed) systems. The presence of the halogen will certainly mitigate the flammability hazards, such as combustion energy and flammability limits, compared with the pure hydrocarbons. The azeotropic composition of the refrigerant mixtures in this study is confirmed in the test cell by noting that the mixture is at a higher saturation pressure than either of the components (Morrison, 1992).

The empirical quantification of the relative performance factors, particularly COP, volumetric capacity, and flammability limits of two such azeotropes are the subject of this paper.

2. EXPERIMENTAL PROCEDURES

2.1. Description of the Heat Pump Performance Test

Mini-breadboard heat pump test rig is composed mainly of compressor, condenser, expansion valve, and evaporator, as shown in Fig. 1. The reciprocating compressor and manually adjusted needle valve expansion device are used in

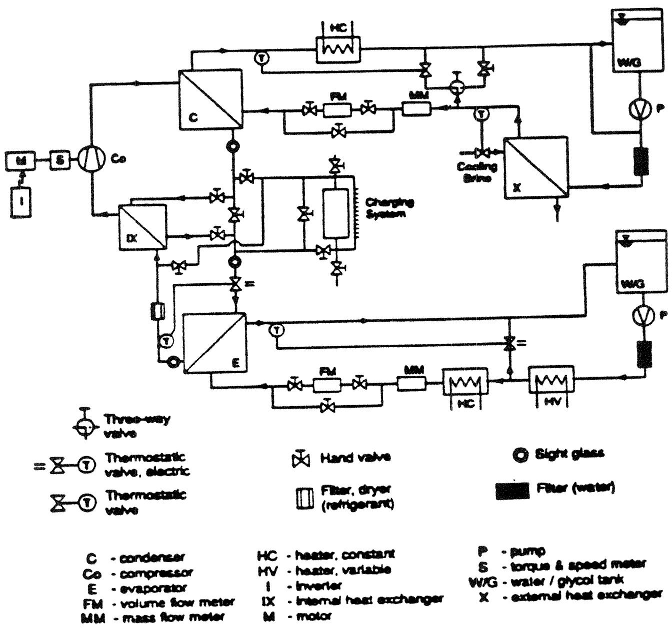

Fig. 1 Schematic diagram of mini breadboard heat pump test rig

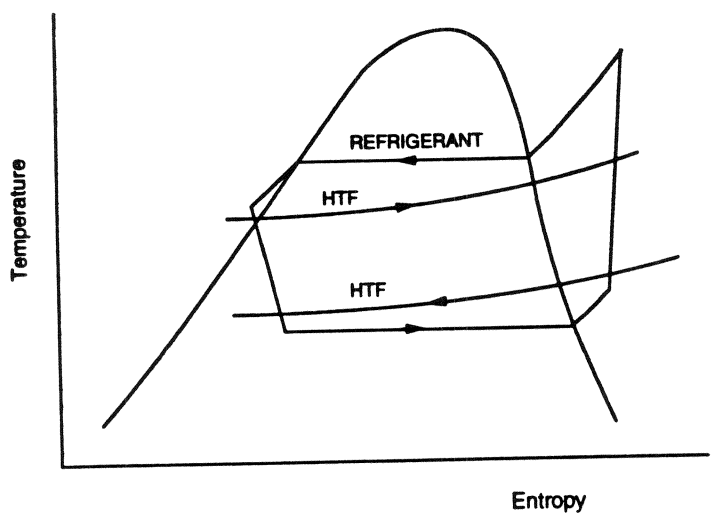

Fig. 2 Thermodynamic cycle of heat pump system with secondary heat transfer fluids (HTF: Heat Transfer Fluid)

the system, and the condenser and evaporator are tube-in-tube counterflow type heat exchangers. The refrigerant flows inside the inner tube of heat exchangers and a water/ethylene glycol mixture is pumped through the annulus. Liquid-line/suction-line heat exchanger(LSHX) is installed so that the refrigerant can flow either to the expansion device or through this heat exchanger and then to the expansion device. The liquid line/suction line heat exchanger can be used to subcool the condensed liquid refrigerant further by the low temperature refrigerant vapor leaving the evaporator and, at the same time, to superheat the suction vapor entering the compressor. The thermodynamic cycle for a heat pump is shown schematically in Fig. 2.

The test conditions in this study are based upon the high temperature cooling or heating conditions described in the ASHRAE Standard 116 (ASHRAE, 1983). The outlet

Table 1 High temperature cooling and heating conditions

Position \ Condition	High Temp. Cooling(°C)	High Temp. Heating(°C)
Condenser Inlet	35.0	21.1
Condenser Outlet	43.2*	VFRE
Evaporator Inlet	26.7	8.3
Evaporator Outlet	14.4*	VFRC

VFRC : Volume flow rate of heat transfer fluid in condenser
VFRE : Volume flow rate of heat transfer fluid in evaporator
* : Estimated value

temperatures of heat transfer fluids are picked based on the previous experiments (Pannock & Didion, 1992), and are shown in Table 1. For the high temperature heating condition, inlet temperatures are chosen as in the ASHRAE standard and outlet temperatures are obtained based on the same flow rates of heat transfer fluids used in the high temperature cooling tests. The heating mode tests are conducted with reversed heat transfer fluid flow rates, that is, the evaporator flow rate for the cooling condition is the same as the condenser flow rate for the heating condition; the condenser flow rate for cooling condition is the evaporator flow rate for heating condition.

In order to obtain comparable test data, condenser subcooling (3°C) and evaporator superheating (14°C for cooling; 8°C for heating) are held constant for all tests. To obtain these conditions, the expansion valve opening as well as the amount of refrigerant charge are adjusted. These conditions are maintained for all operating conditions. The compressor speed is kept constant at 1000 rpm for every refrigerant by use of an inverter. In this way the compressor "size" was effectively held constant throughout all tests, thus simulating "drop-in" applications.

For the measurement of the refrigerant mixture composition, a small amount of vapor sample is extracted from the compressor discharge line during the steady state operation and evaluated with the gas chromatograph.

2.2. Description of Flammability Test

Flammability test apparatus, shown in Fig. 3, is simi. to the apparatus described in ASTM-681 (ASTM, 1992). A the tests are recorded with a video camera. The tests are conducted at room temperature and pressure conditions, as required by ASHRAE Standard 34 (ASHRAE, 1992). The room temperature is kept 21°C (± 1.5°C) and the pressure inside the test cell is kept at an atmospheric pressure.

3. RESULTS AND DISCUSSION

3.1. Performance of the Refrigerants in the Heat Pump

It is reasonable to categorize the alternates into two capacity groups, of which the first is R-290/134a and R-290

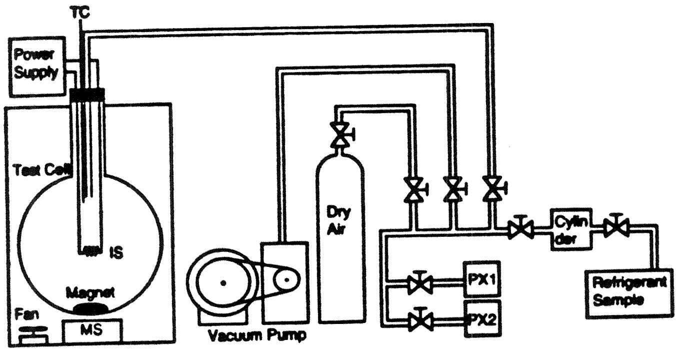

Fig. 3 Schematic diagram of flammability test apparatus (TC: thermocouple, IS: ignition device, MS: magnetic stirrer, PX1: pressure transducer, PX2: vacuum gauge)

and the second, R-134a/600a and R-134a. The performances of R-290/134a are compared with R-22, R-290, and those of R-134a/600a are compared with R-12 and R-134a.

High temperature cooling test (T_c = 35.0°C, T_e = 26.7°C). The performance results of all the fluids are presented in Fig. 4. The capacity is the amount of heat ($\dot{Q}_r$) that is removed from the water/glycol stream within the evaporator. The coefficient of performance (COP) is defined as this capacity ($\dot{Q}_r$) divided by the mechanical work input to the compressor ($\dot{W}$).

The capacity of R-290/134a is greater than that of R-22 or R-290. The cycle capacity is closely related to the density of vapor entering the compressor and the latent heat at the evaporator pressure. The density of vapor at compressor inlet of R-290/134a is smaller than R-22, but larger than R-290. The latent heat at evaporator pressure of R-290/134a is larger than R-22, but smaller than R-290. The cycle capacity is related to the product of the above two values and that of R-290/134a reveals to be greater than that of R-22 and R-290. The capacity of R-134a/600a is greater than that of R-12 or R-134a, and the reason is similar as in the previous case; the density of vapor at compressor inlet of R-134a/600a is smaller than R-12, but larger than R-134a, and the latent heat at evaporator pressure of R-134a/600a is larger than R-12 and similar to R-134a (Gallagher et al., 1991).

The coefficient of performance for R-290/134a is smaller than that for R-22 and R-290. This may be attributed to an increase in work per unit volume flow (constant rpm tests) which, in turn, is largely influenced by the suction pressure. The suction pressure of R-290/134a is higher than that of R-22 and R-290, which makes the work required in compression of R-290/134a become greater than R-22 and R-290. The ratio between the capacity and work, i.e., coefficient of performance for R-290/134a reveals to be smaller. For R-134a/600a, the coefficient of performance is higher than that for R-12 and R-134a. The suction pressure for R-134a/600a is higher than R-12 and R-134a, therefore the work required in compression of R-134a/600a becomes greater. Even though the work for R-134a/600a is higher,

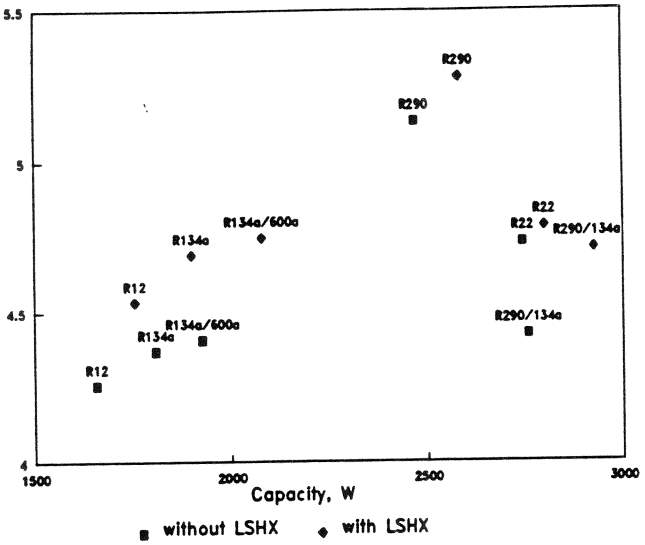

Fig. 4 Cooling COP with respect to cycle capacity at high temperature cooling condition

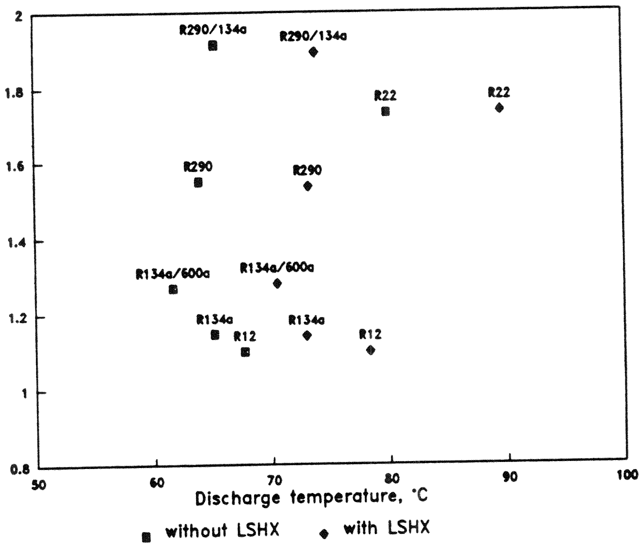

Fig. 5 Discharge pressure with respect to discharge temperature at high temperature cooling condition

the ratio between the capacity and work for this mixture reveals to be still higher than the other refrigerants.

The discharge temperature and pressure are important factors because they influence lubricant stability and system life. As shown in Fig. 5, the discharge temperature of R-290/134a is lower than that of R-22 and slightly higher than R-290. That of R-134a/600a is lower than that of R-12 and R-134a. Since for all tests the suction temperature is almost the same, the discharge temperature is largely a function of the specific heat of vapor. For example, the specific heat of R-290/134a is larger than that of R-22, so the discharge temperature is lower, which is a desirable condition.

The discharge pressure of R-290/134a is somewhat higher than that of R-22 and R-290, and that of R-134a/600a is slightly higher than that of R-12 and R-134a. As the condensing temperature is almost the same for all tests, the discharge pressure is related to vapor pressure. As the vapor pressure of R-290/134a is higher than R-22, R-290 and that of R-134a/600a is higher than R-12, R-134a, the discharge pressures are higher. The discharge pressure for all cases are revealed to be lower than the commercial design pressure limit, i.e., about 2.6 MPa.

High temperature heating test (T_c = 21.1°C, T_e = 8.3°C). The cycle capacity($\dot{Q}_h$) of R-290/134a is greater than that of R-22 and R-290. This can be attributed to the latent heat in the condenser pressure and the mass flow rate of refrigerant, of which the latter is related to the density of vapor phase at compressor inlet under constant compressor speed condition. In this test condition, the densities of vapor phase at compressor inlet are the same as explained before and the heating effect at condenser pressure of R-290/134a is larger than R-22, but smaller than R-290, and as a result the cycle capacity of R-290/134a becomes greater than that of R-22 and R-290. The capacity of R-134a/600a is greater than that of R-12 or R-134a, and the reason is similar as in the previous case.

The coefficient of performance for R-290/134a is smaller than that for R-22 and R-290, which is shown in Fig. 6. Although the heating capacity of this mixture is greater than that of the other refrigerants, the work required to compress this refrigerant mixture is much greater. For R-134a/600a, the coefficient of performance is higher than that for R-12 and R-134a. Even though the required compressor work is greater for R-134a/600a, the ratio between the capacity and work remains still higher than that for the other refrigerants.

The discharge temperature shown in Fig. 7 represents the similar pattern as in the previous test condition. The discharge temperature of R-290/134a is even lower than that for R-22 and slightly higher than that for R-290. Considering that the suction temperature is almost the same for all tests of the same test condition, the higher discharge temperature is expected for the refrigerant with lower specific heat of vapor phase. The discharge temperature of R-134a/600a is lower than that of R-12 and R-134a.

The discharge pressure of R-290/134a is somewhat higher than that of R-22 and R-290, and that of R-134a/600a is slightly higher than that of R-12 and R-134a. The results are shown in Fig. 7. All the discharge pressures of this test condition are lower than those of the previous high temperature cooling tests.

Liquid-line/suction-line heat exchange. The high temperature cooling and heating test results with liquid-line/suction-line heat exchange (LSHX) are shown in Figs. 4 through 7. The LSHX subcools the liquid from the condenser with the suction vapor from the evaporator. The benefit with LSHX depends on both operating conditions and refrigerant properties. It is an advantage that the application of LSHX always results in an increase in system capacity because of the subcooling effect. Whether the LSHX improves the coefficient of performance is a function of the vapor heat capacity (Domanski et al., 1992). All the test conditions with LSHX are maintained the same as the previous cases without LSHX and the compressor speed is also kept by 1000 rpm.

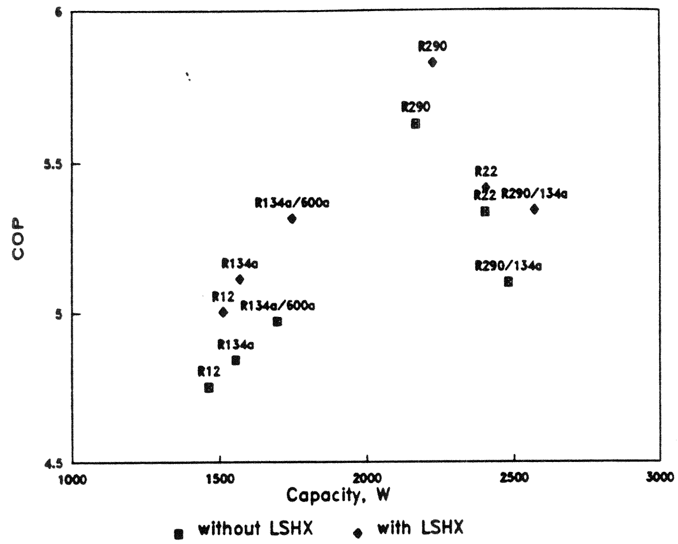

Fig. 6 Heating COP with respect to cycle capacity at high temperature heating condition

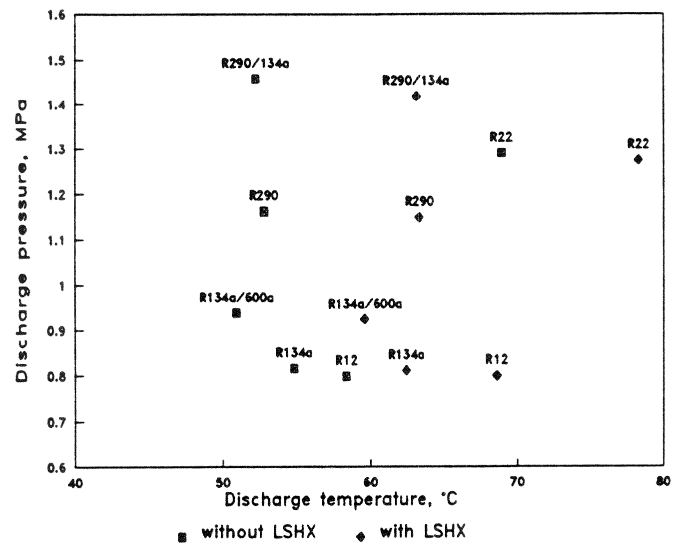

Fig. 7 Discharge pressure with respect to discharge temperature at high temperature heating condition

For the R-290/134a mixture of which the vapor heat capacity is greater than R-22 and R-290, thus the increase in cycle capacity and COP is higher than that of R-22 and R-290 at both test conditions. For R-134a/600a with greater heat capacity of vapor phase than R-12 and R-134a, both the capacity and COP increase at the high temperature cooling condition is higher than that of R-12 and R-134a, but almost the same as that of R-12 at the high temperature heating test.

The discharge temperature becomes higher for all tests with LSHX, which is expected when any refrigerant's superheat is increased. The results show that the highest discharge temperature is obtained for R-22 in every case, which is a result of it having the lowest vapor heat capacity. The discharge temperatures for other refrigerants are lower than that of R-22 because they are more complex molecules and, therefore, have a higher heat capacity. The discharge pressure is almost the same for all tests with LSHX as the tests without LSHX. As shown in Figs. 5 and 7, the average difference between the two cases is less than 1 % for all test conditions.

3.2. Flammability Test of Azeotropic Refrigerant Mixtures

It is usually desired that the refrigerant used in commercial applications is nonflammable. However, history as well as recent studies suggest that pure propane (R-290) has some merit as a refrigerant (Kramer, 1991) and, of course, ammonia has been widely used in industrial applications throughout the history of refrigeration. Investigations into the use of propane in domestic refrigerators have included energy consumption tests, combustion tests, fire tests, and etc. (James & Missenden, 1992). Their conclusion is that a refrigerator with propane is capable of similar performance as with R12 with appropriate design changes, and the explosion and fire risks are small. The main concept in this study about flammability is to add nonflammable R-134a to flammable hydrocarbons to reduce flammability of the hydrocarbon and retain the thermodynamic and practical advantages of the single component refrigerant. In this study, the composition of mixtures are chosen so as to have azeotropic behavior and the flammability tests are done for that specific composition.

The flammability limits are found based upon visual observation of all the recorded flammability tests on video tapes. In this study, flammable mixture is represented by the composition where the flame propagates horizontally from the ignition source after being mixed with air and ignited. The flammability limits of R-290/134a (45/55) are found to be 2.9-11.0 % by volume in refrigerant/air mixture. And those of R-134a/600a (80/20) are 3.9-13.3 % by volume in refrigerant/air mixture. These may be compared to their respective pure hydrocarbons R-290 and R-600a, where the limits are 2.1-9.6 % and 1.7-9.7 % by volume respectively (Richard & Shankland, 1992). It is noteworthy that the lower limit is higher for both mixtures than that for pure hydrocarbons. Although the azeotropic mixtures remain flammable, they are less flammable than their pure hydrocarbon compounds. It is well-known that the presence of halogen compound may show flame inhibition characteristics (Biordi et al., 1973; Ho et al., 1992). One might also reason that the presence of the relatively high heat capacity nonflammable halogen will reduce the combustion energy of the hydrocarbon.

3.3. Other Discussions

Tests for this report are performed using a constant compressor speed criterion. In a practical sense, the constant compressor speed test tends to simulate the drop-in case of performance of a system by changing the refrigerant in a system sized for the CFC. An alternative test approach is one of constant heat flux in the evaporator for all refrigearnts in which capacity is maintained constant by varying compressor speed; hence the evaluation has two component changes, refrigerant and compressor speed. Constant compressor speed tests overstate the efficiency of low volumetric capacity refrigerants as a result of lower heat fluxes and consequent reduced refrigerant-to-heat sink temperature differences. Constant heat flux tests tend to understate the efficiency of low volumetric capacity refrigerants as a result of increases refrigerant pressure drop (particularly on the low side) with increased compressor speed. The Comparisons in this report are made in two capacity groups, one near R-12 and the other near R-22. It is felt that the capacity range in each group is sufficiently small that test results by either criterion would be comparable since the two test criteria are identical when comparing refrigerants of identical volumetric capacity. However in interpreting the results it is well to be alert to this bias in favor of low capacity refrigerants where comparisons are made to disparate refrigerants.

It is desirable for a refrigerant to be completely miscible with refrigerant oil while in the liquid state. Without this characteristic, refrigerant oil will tend to accumulate in the liquid circuitry of the system where velocity is low, and the separated oil cannot return to the compressor. The HFC refrigerants, which are most frequently proposed as environmentally safe alternatives to CFC refrigerants, do not provide such oil solubility with mineral oils because they don't have any chlorine atom which provides the necessary solubility link. As a result, the industry is developing a new family of ester based lubricants, which are attaining some success, but do not yet provide the confidence of a trouble free performance nor the ability to allow for a drop-in replacement for existing equipment. Addition of a hydrocarbon such as propane or isobutane even in small amounts is known to provide such oil solubility (Bennett et al., 1966; Enjo & Fujiwara, 1975; Enjo & Noguchi, 1985). The mixtures in this study will provide oil solubility with mineral oil that R-134a or other HFCs would not have, and thus offer the potential to be a drop-in alternative.

A final point is about the R-290 test results relative to R-22. Although the thermodynamic rating for the coefficient of performance of R-290 is less than that of R-22, the tests in this study show the opposite results. We should note that all the tests conducted are under the constant compressor rpm criteria. The capacity of R-290 is lower than that of R-22, thus the heat exchanger loading decreases and so does the average temperature difference in heat exchanger. The liquid viscosity of R-290 is approximately 65% of R-22 in the test range, so R-290 has a significantly lower saturation pressure drop (about half of R-22) through the heat exchangers. The liquid thermal conductivity of R-290 is approximately 10 % higher than that of R-22, therefore it is thought that the overall heat transfer coefficient is higher and the effective average temperature difference in the heat exchanger for R-290 decreases. These factors result in a better match between the water and refrigerant temperature profiles, which finally give higher COP values than that from the simulation results.

4. CONCLUDING REMARKS

In this paper, heat pump performance tests are conducted for two azeotropic refrigerant mixtures of R-134a (1,1,1,2-tetrafluoroethane) with R-290 (Propane) and R-600a (Isobutane): R-290/134a (45/55), R-134a/600a (80/20). Major reasons in selecting these mixtures are azeotropy (no temperature change during phase change), increased oil solubility, and reduced flammability compared with hydrocarbon. The tests are done at constant compressor speed condition to simulate the performance of several refrigerants as a 'drop-in' for the current system. The performance characteristics of R-290/134a are compared with pure R-22, R-290 and those of R-134a/600a with R-12, R-134a at specific test conditions including cases using liquid-line/suction-line heat exchange. In addition to this, flammability tests are performed to get the flammability limits of azeotropic mixtures in this study.

The cycle capacity of R-290/134a is greater than that of R-22 and R-290. And the capacity of R-134a/600a is greater than that of R-12 or R-134a. In every case, the coefficient of performance for R-290/134a is lower than that for R-22 and R-290. For R-134a/600a, the COP is higher than that for R-12 and R-134a. Results show that the discharge temperature of R-290/134a is lower than that of R-22 and slightly higher than that of R-290. The discharge temperature of R-134a/600a is lower than that of R-12 and R-134a. The R-290/134a has a higher discharge pressure than R-22 and R-290, and R-134a/600a slightly higher than R-12 and R-134a.

The flammability limit of R-290/134a is found as 2.9-11.0 % by volume and that of R-134a/600a is 3.9-13.3 % by volume. Although the azeotropic mixtures remain flammable, they are less than their pure hydrocarbon components.

Even though the coefficient of performance of R-290/134a is slightly lower than that of R-22 and R-290, considering its greater capacity and the flammability of R-290, R-290/134a can be a possible substitute for R-22. As regards the R-134a/600a mixture, it can be also a possible substitute for R-12 because of its higher capacity and coefficient of performance.

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